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Ultrahigh Molecular Weight Polyethylenes (UHMWPE)

Harvey L. Stein, Hoechst Celanese Corporation

ULTRAHIGH MOLECULAR WEIGHT POLYETHYLENE (UHMWPE) is a linear, low-pressure, Ziegler-type-catalyst, polyethylene resin. Its weight-average molecular weight of 4×10^6 is approximately ten times that of high molecular weight high-density polyethylene (HDPE) resins. The extremely high molecular weight of this resin, which is commercially available in grades ranging from 3×10^6 to 6×10^6, yields several unique properties.

UHMWPE has both the highest abrasion resistance and highest impact strength of any plastic. In fact, a 25 mm (1 in.) thick slab can stop a 0.38 caliber pistol slug at 150 mm (6 in.). Figures 1 and 2 show a comparison of abrasion and impact strengths with those of other materials.

Combined with abrasion resistance and toughness, the low coefficient of friction of UHMWPE yields a self-lubricating, nonstick surface. Static and dynamic coefficients of friction are significantly lower than steel and most plastic materials (Table 1).

The basic chemical unit of UHMWPE is $—CH_2—$. Thus, a 4×10^6 molecular weight resin contains approximately 285×10^3 carbon atoms or units in the polymer chain. The insolubility of UHMWPE makes size exclusion chromatography (SEC) impractical. Molecular weight is therefore determined by the measurement of dilute-solution viscosity, as detailed in ASTM D 1601 and D 4020 (Ref 1, 2). With these procedures, UHMWPE is defined as a substantially linear polyethylene (PE) having a relative viscosity of 2.3 or greater at a concentration of 0.05% at 135 °C (275 °F) in decahydronaphthalene. The nominal molecular weight is approximated using the Mark-Houwink equation $M = 5.37 \times 10^4 (IV)^{1.37}$, where IV represents intrinsic viscosity. This method is not valid on thermally processed materials because of inadequate solubility and possible cross linking. However, a relative indication of molecular weight can be determined by sand slurry tests of molded or extruded specimens.

As molecular weight increases from 3×10^6 to 6×10^6, abrasion resistance improves significantly (by approximately 30%), whereas impact strength decreases from 140 to 80 kJ/m² (67 to 38 ft · lbf/in.²). By comparison, most HDPE grades range from 13 to 40 kJ/m² (6 to 19 ft · lbf/in.²). A special test specimen had to be devised to determine the toughness of UHMWPE because no break occurs with conventional test methods. The ASTM D 256 (Ref 3) Izod impact test specimen was modified with two opposing 15° notches rather than the standard 45° notch. Double-notched Izod values typically exceed 1.6 kJ/m (30 ft · lbf/in.) notch for UHMWPE. Figures 3 and 4 show the relationship between notched impact strength and temperature. Most other mechanical, thermal, and physical properties remain essentially constant throughout the molecular weight range of UHMWPE.

Typical costs for truckload quantities of standard grade virgin resins were \$2.30/kg (\$1.06/lb) at the end of 1987. Because of the relatively low density of 0.93 g/cm³, the price per cubic inch is currently lower than for any other engineering resin. Available packaging includes bags (25 kg, or 55 lb), drums (90 kg, or 200 lb), containers or bulk packs (360 kg, or 800 lb), and railcars (63.5×10^3 kg, or 140×10^3 lb).

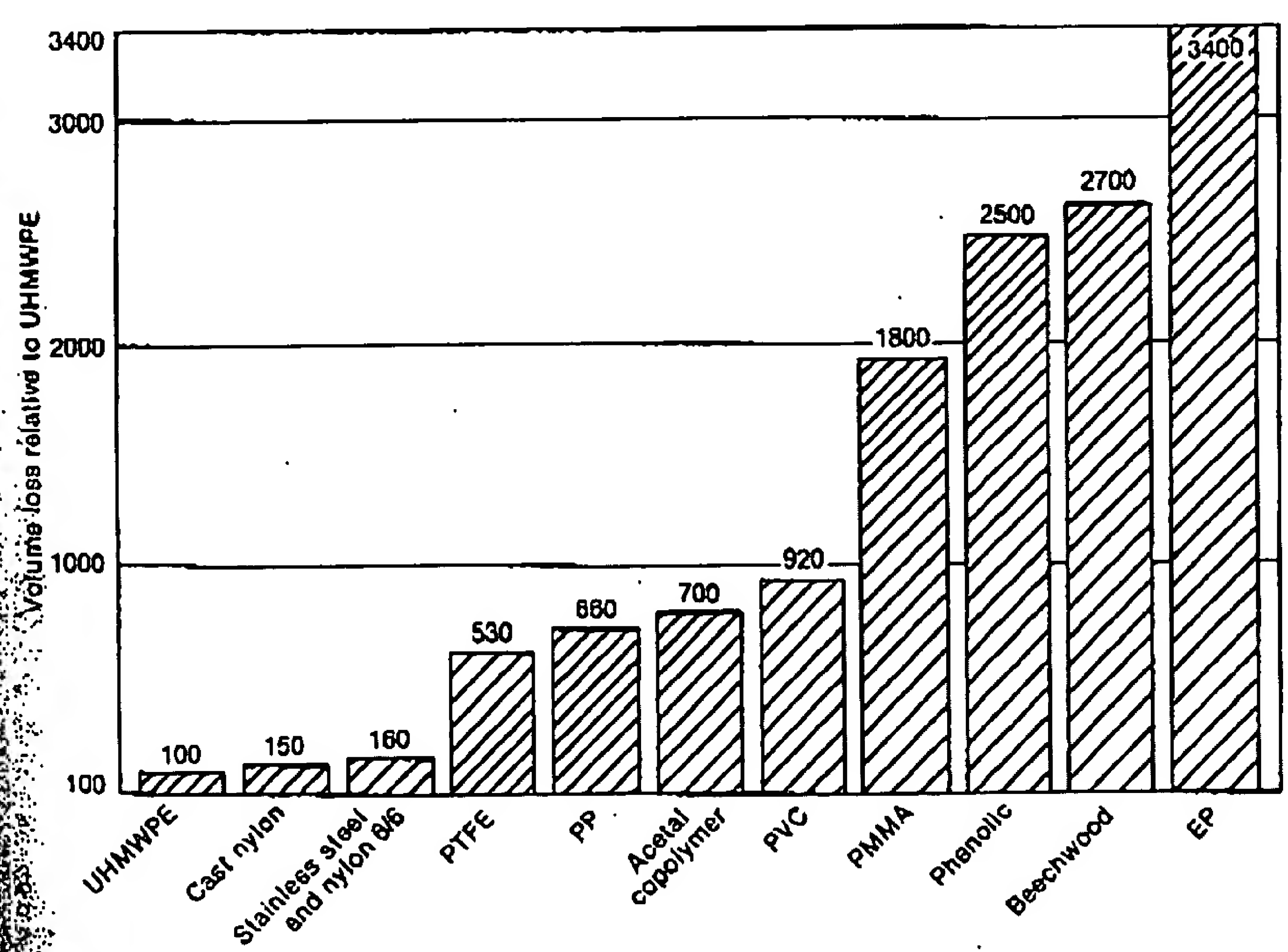

Fig. 1 Comparative abrasion resistance of different engineering resins. PTFE, polytetrafluoroethylene; PVC, polyvinyl chloride; PMMA, polymethyl methacrylate; EP, epoxy

Applications

Because of its self-lubricating, nonstick, lightweight, and wear-resistant characteristics, UHMWPE has been used for many years in the bulk material handling (grain, cement, gravel, and aggregate) and ore/coal mining industries. Applications include liners for silos, hoppers, dump trucks, railcars, and chutes; conveyor troughs and flights;

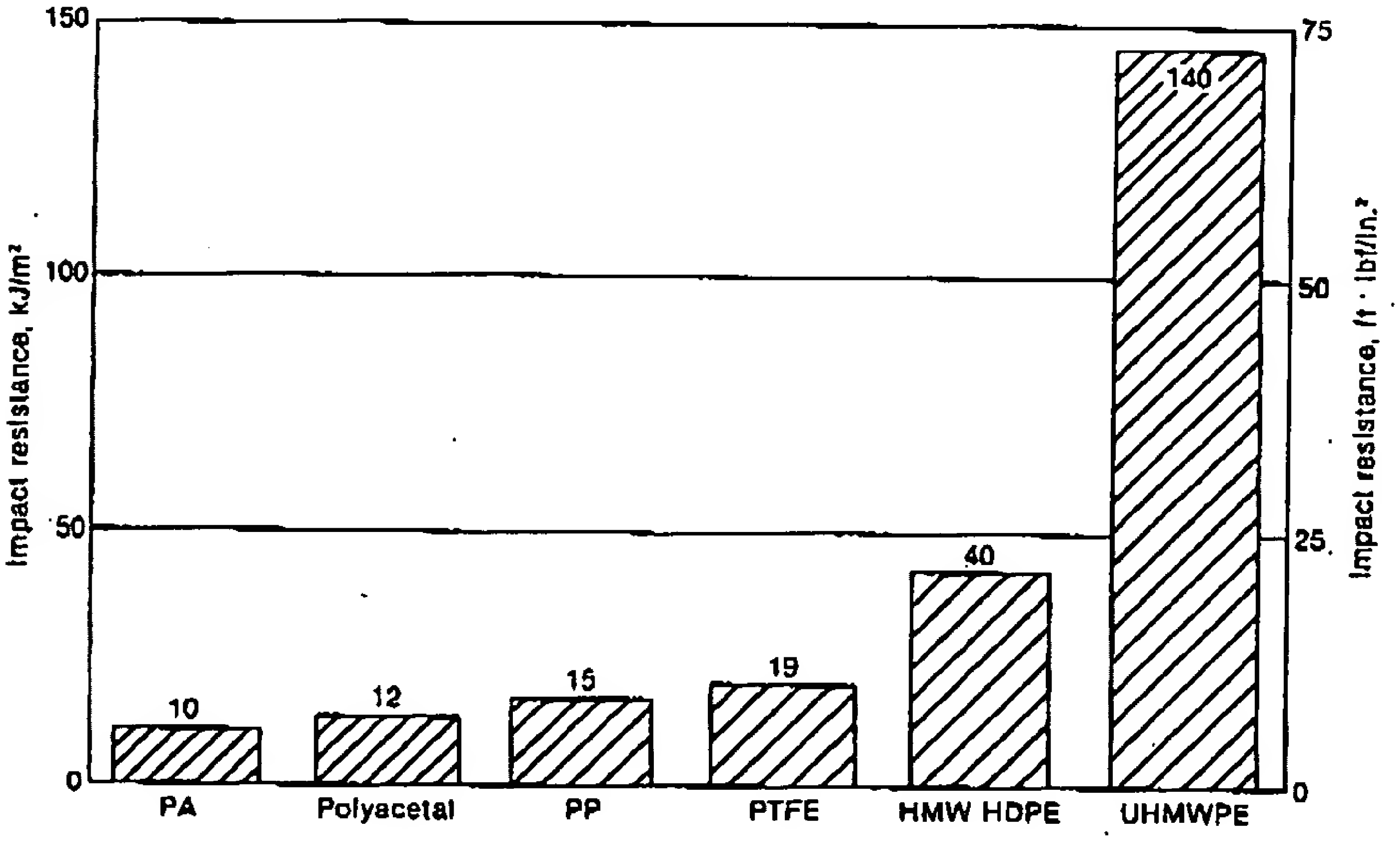

Fig. 2 Comparative impact resistance of different engineering resins

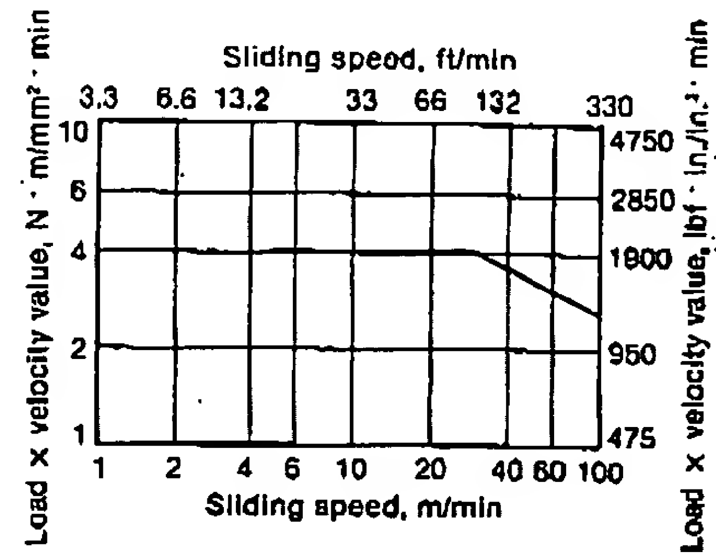

Fig. 5 Load limits for unlubricated bearings made from UHMWPE

Tabl 1 Comparison of dynamic coefficient of friction on polished steel

Resin	Dry	Water	Oil
UHMWPE......	0.10–0.22	0.05–0.10	0.05–0.08
PA...........	0.15–0.40	0.14–0.19	0.02–0.11
Nylon 6/6......	0.15–0.40	0.14–0.19	0.02–0.11
PA/molybdenum disulfide.....	0.12–0.20	0.10–0.12	0.08–0.10
Polytetrafluoroethylene.....	0.04–0.25	0.04–0.08	0.04–0.05
Acetal copolymer....	0.15–0.35	0.10–0.20	0.05–0.10

PA, polyamide

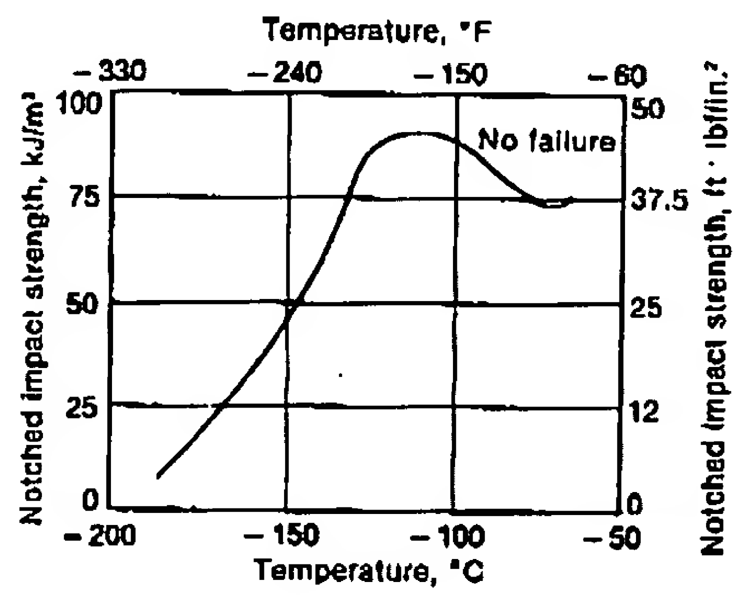

Fig. 4 Notched impact strength of UHMWPE as a function of temperature, based on a single 45° V-notch

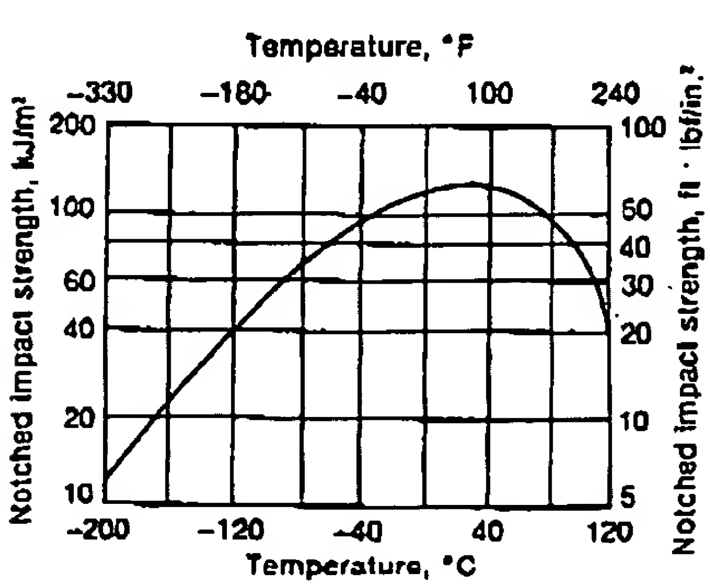

Fig. 3 Notched impact strength of UHMWPE as a function of temperature, using sharp V-notched test bar with double 15° V-notch

wear strips; slide plates; and unlubricated bearings and bushings. Additional benefits of UHMWPE include increased product flow, reduction or elimination of caking (particularly in wet or icy conditions), noise abatement, and reduced energy consumption.

The absorption capacity for shock stress is extraordinary, even at temperatures approaching absolute zero. Thus, cryogenic and cold-weather applications are ideal for UHMWPE, whereas lower molecular weight HDPE resins could fail. Seals, pistons, and pumps perform satisfactorily in liquid hydrogen pumps at −253 °C (−423 °F).

The textile industry uses UHMWPE because of its excellent impact resistance and sound-dampening characteristics. It is used in highly stressed parts, including loom pickers, shuttles, sticks, straps, caps, buffers, gears, pinions, and small rollers.

Medical applications include prostheses and surgical supports, because the mechanical properties of this material have excellent biocompatibility with human tissue. All virgin UHMWPE grades are in compliance with U.S. Food and Drug Administration regulations and have received U.S. Department f Agriculture approval.

The food, beverage, and pharmaceutical industries use UHMWPE extensively because oil and grease can be eliminated from most bearing applications. Furthermore, the growth of fungus and bacteria is discouraged because the material is nonporous. Common applications include bottling plant star wheels and guard rails.

Other applications include pump impellers, pump housings, valve seats, and valve gaskets for the chemical process industry; doctor blades, suction box covers, and chain conveyor wear plates for the pulp and paper industry; ski bottom surfaces, snowmobile drive sprockets, golf ball cores, and bowling-alley and ice-skating rink surfaces for the recreational industry; and dock fenders for the maritime industry. The compaction and sintering process can produce porous parts, including marking pen nibs and filters for blood, home faucets, and industrial use.

Metal shafts can rotate freely in UHMWPE bushings despite misalignment or the presence of sand, dust, or dirt particles. In the design of bushings and bearings, dry PV (pressure times velocity) values should be limited to 4 N · m/mm² · min (1900 ft · lbf/in.² · min), whereas lubricated applications range from 6 to 7 N · m/mm² · min (2850 to 3330 ft · lbf/in.² · min) (Fig. 5). Load and speed limits are 10 MPa (1.5 ksi) and 120 m/min (400 ft/min), respectively. Bearing temperatures below 40 °C (104 °F) should be maintained.

Future Trends. Since the time that UHMWPE fibers were first introduced in the military and recreational industries, new applications have developed, such as nautical rope and sails. The introduction of injection molding will permit entrance into new areas in which high part volume must be economically produced.

Family Characteristics

The extremely high molecular weight of UHMWPE makes it a unique material. Its special characteristics, some of which have already been described, include:

- Outstanding abrasion resistance
- Highest impact resistance of any plastic material
- Low coefficient of friction
- Nonstick, self-lubricating surface
- Good chemical resistance
- Negligible water absorption
- Excellent properties at cryogenic conditions

  Stress-cracking resistance exceeding 3000 h in surfactants

  Energy absorption and sound-dampening properties
- Excellent dielectric and insulating properties

The outstanding characteristics of this material can be maintained from −269 °C (−452 °F) to 90 °C (194 °F) and even higher for short periods of time. Because the resin does not melt-flow or liquify at its 138 to 142 °C (280 to 289 °F) melting point, the resin retains excellent dimensional stability at temperatures up to 200 °C (392 °F). In a special application described in Ref 4, UHMWPE was used at temperatures up to 450 °C (840 °F) for sulfuric acid spray nozzles, because rapid carbonization of the surface occurred, forming a protective skin.

Outdoor ultraviolet (UV) light can degrade this material, as well as other olefinic materials, leading to cracking within a 1 year period, unless UV stabilizers are added during processing. An allowance for creep, or cold flow (such as 2% at 2 MPa at 20 °C, or 0.290 ksi at 68 °F), should be made. Creep properties under compressive stress are shown in Fig. 6. Other properties of the processed resin are listed in Tables 2 and 3.

Chemical resistance to aggressive media, including most strong oxidizing agents, is excellent. Exposure to aromatic and halogenated hydrocarbons results in only slight surface swelling if moderate temperature levels are maintained.

Processing Parameters. The extremely high processing viscosities resulting from high molecular weight require special processing procedures because the resin does not exhibit a measurable melt index and is more like an amorphous solid. The most common methods for fabrication of UHMWPE are ram extrusion and compression molding. In both cases, the individual UHMWPE particles are fused into an apparent solid, but microscopically they remain as discrete particles, although there is a level of segmented diffusion between particles. Ram extrusion is accomplished by continuously feeding resin through a hopper into the extruder throat and then packing the material in frequent intervals with a reciprocating plunger, thus removing the air phases. The compressed powder then moves through heated zones, where it is fused. The cross-section of the barrel or die corresponds to the profile of the product. Production rates are influenced by the hydraulic system heater capacity, the die length, and the strength of the construction materials. Typical extrusion rates are 10 to 20 kg/h (22 to 44 lb/h). Controller set-point temperatures are 160 to 230 °C (320 to 446 °F).

Compression molding of sheets ranging from 1.2 × 2.4 m (4 × 8 ft) to 1.5 × 3.7 m (5

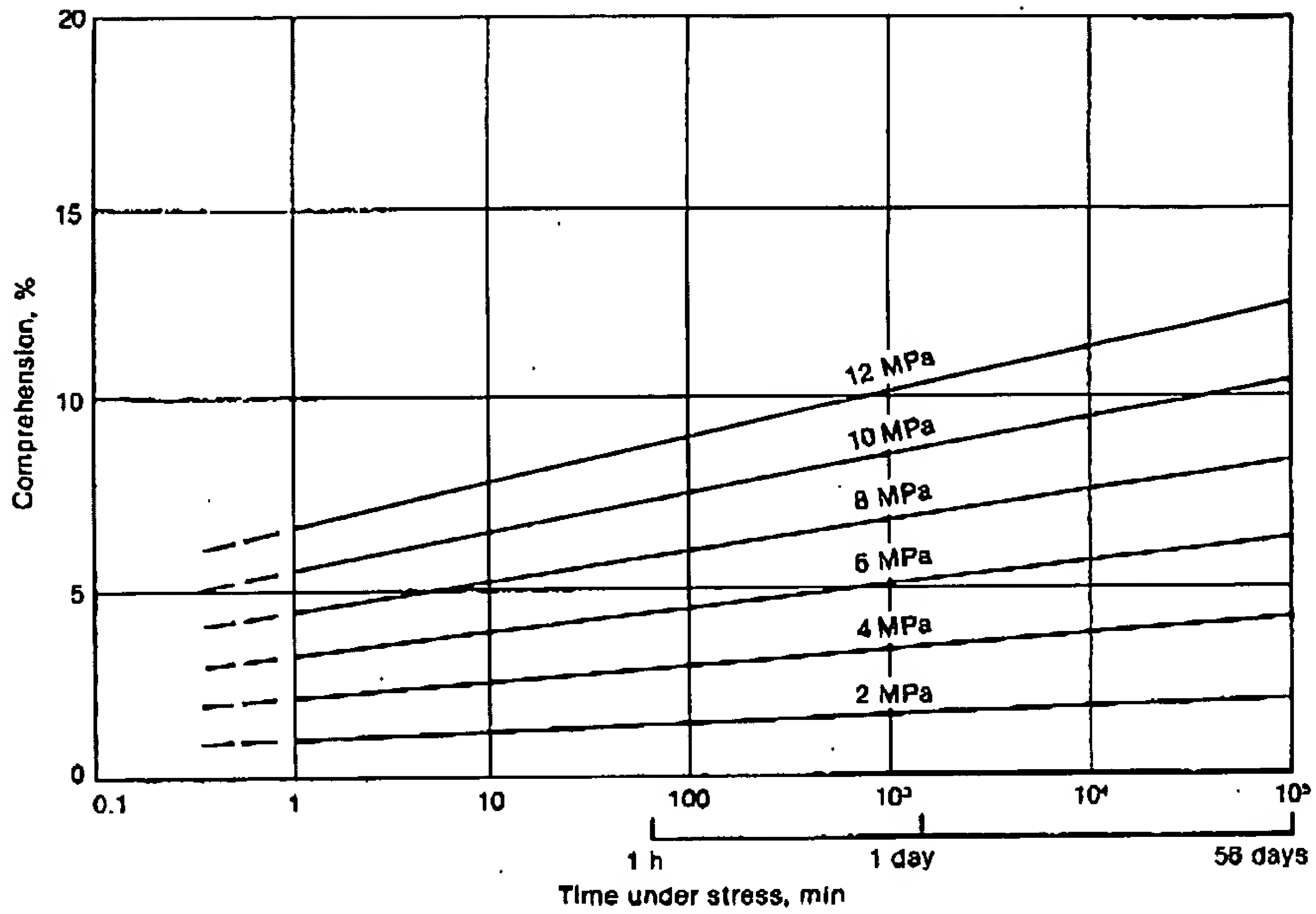

Fig. 6 Creep properties of UHMWPE under varying compressive stress rates, measured at 20 °C (68 °F)

Table 2 UHMWPE properties

Property	Typical values	ASTM test method
Mechanical		
Density, g/cm^3	0.926–0.934	D 792
Tensile strength at yield, MPa (ksi)	21 (3.1)	D 638
Tensile strength at break, MPa (ksi)	48 (7.0)	D 638
Elongation at break, %	350	D 638
Young's modulus, GPa (10^6 psi)		
At 23 °C (73 °F)	0.69 (0.10)	D 638
At −269 °C (−450 °F)	2.97 (0.43)	D 638
Izod impact strength, kJ/m (ft · lbf/in.) notch		
At 23 °C (73 °F)	1.6 (30)	D 256(a)
At −40 °C (−40 °F)	1.1 (21)	D 256(a)
Hardness, Shore D	62–66	D 2240
Abrasion resistance	100	...
Water absorption, %	Nil	D 570
Relative solution viscosity, dL/g	2.3–3.5	D 4020
Thermal		
Crystalline melting range, powder, °C (°F)	138–142 (280–289)	Polarizing microscope
Coefficient of linear expansion, 10^{-4}/K		
At 20 to 100 °C (68 to 212 °F)	2	D 696
At −200 to −100 °C (−330 to −150 °F)	0.5	D 696
Electrical		
Volume resistivity, Ω · m	$>5 \times 10^{14}$	D 257
Dielectric strength, kV/cm (V/mil)	900 (2300)	D 149
Dielectric constant	2.30	D 150
Dissipation factor, × 10^{-4}		
At 50 Hz	1.9	D 150
At 1 kHz	0.5	
At 0.1 MHz	2.5	
Surface resistivity, wt% carbon black, Ω		
0.2% for color	$>10^{14}$	D 257
2.5% for UV protection	10^{13}	D 257
6.5% for antistatic applications	10^5	D 257
16.7% for conductive applications	10^3	D 257

(a) Samples had two notches (15° ± ½°) on opposite sides to a depth of 5 mm (0.20 in.).

Table 3 UHMWPE chemical resistance of dumbbell-type test specimens after 30 days

+, resistant (mechanical properties not appreciably affected); —, not resistant (decrease in yield stress and ultimate tensile strength greater than 20%; X, limited resistance (decrease in yield stress and ultimate tensile strength less than 20%

Reagent	Temperature 20 °C (68 °F)	50 °C (120 °F)	80 °C (175 °F)
Inorganic acids			
Chromic acid (80%)	+	+	×
Hydrochloric acid (concentrated)	+	+	+
Hydrocyanic acid	+	+	
Hydrofluoric acid	+	+	
Nitric acid (concentrated)	—	—	—
Nitric acid (50%)	×	—	—
Nitric acid (20%)	+	+	×
Phosphoric acid (85%)	+	+	+
Sulfuric acid (concentrated)	+	—	—
Sulfuric acid (75%)	+	×	×
Sulfuric acid (50%)	+	+	+
Alkalies			
Aqueous ammonia	+	+	
Potassium hydroxide solution	+	+	+
Sodium hydroxide solution	+	+	+
Aqueous solutions of inorganic salts			
Aluminum chloride	+	+	+
Ammonium nitrate	+	+	+
Bleaching powder	+	+	+
Calcium chloride	+	+	+
Sodium carbonate	+	+	+
Sodium chloride	+	+	+
Sodium hypochlorite	+	+	+
Zinc chloride	+	+	+
Organic acids			
Acetic acid (99%)	+	+	×
Acetic acid (10%)	+	+	+
Butyric acid	+	+	
Citric acid	+	+	+
Formic acid	+	+	
Oleic acid	+	+	×
Hydrocarbons and halogenated hydrocarbons			
Benzene	×	×	
Carbon tetrachloride	×		
Cyclohexane	+	+	
Dichloroethylene	—	—	
Diesel oil	+	+	×
n-heptane	+	+	
Petroleum ether	+		
Trichloroethylene	×	—	
Toluene	×	—	
White spirit	+	×	
Xylene	×	×	—
Alcohols, ketones, ester and amines			
Acetone	+	+	
Aniline	+	+	×
Benzyl alcohol	+	+	+
Butyl alcohol	+	+	+
Cyclohexanol	+	+	+
Ethanol	+	+	
Ethyl acetate	+	+	
Ethylene glycol	+	+	+
Glycerine	+	+	+
Lauryl alcohol	+	+	+
Propyl alcohol	+	+	+
Miscellaneous			
Beer/wine	+	+	+
Detergents in aqueous solution	+	+	+
Distilled water	+	+	+
Hydrogen peroxide 30% (perhydrol)	+	+	
Linseed oil/olive oil	+	+	+
Milk	+	+	+
Seawater	+	+	+

× 12 ft) is performed by homogeneous filling of the mold to 2.2 to 2.5 times the desired sheet thickness and then carefully leveling the powder with a straight edge. The powder is then cold compressed for 5 to 10 min at 7 to 10 MPa (1 to 1.5 ksi) to expel air and compact the material. At a minimum of 3.5 to 5 MPa (0.500 to 0.750 ksi), the heat cycle is begun until the entire charge is fused. Pressure is then increased to 10 MPa (1.5 ksi) during cool-down to prevent voids inside the block and sink marks on the surface. Sheets can be subsequently sliced if preheated to 140 to 150 °C (285 to 300 °F) before slicing. After being sliced, sheets are placed between thin aluminum steel plates, reheated to 150 °C (300 °F) and slowly cooled to room temperature to remove processing stresses.

Porous parts are produced by the compaction and sintering method, including vibratory compaction. A cavity is filled with resin and vibrated to ensure uniform packing. The volume is then enclosed and heated to 175 to 205 °C (350 to 400 °F) without pressure, and then cooled. Predictable porosities are attained by careful selection of particle size distribution and bulk density. Resins with extremely low bulk densities (200 to 250 g/L, as opposed to a normal 350 to 500 g/L) are particularly suitable for these applications.

Other fabrication techniques include direct compression molding of parts, hot stamping, forging, and hot plate or spin welding. Injection molding can be performed on most modern reciprocating-screw-type injection molding machines although equipment and mold modifications may be necessary. Careful attention to operating conditions is necessary to prevent the production of degraded parts.

Semifinished parts can be easily sawed, turned, planed, milled, drilled, or punched with standard wood or metal fabricating machines. Sharp tools with wide-tooth spacing are necessary for adequate chip clearance and heat removal.

Adhesion of UHMWPE to substrates is poor, even with surface roughening and heat treatment. The difference between the coefficient of thermal expansion of UHMWPE and those of metals makes mechanical methods of fastening preferable. These include weld washers, stud welds, rivets, and flat-head elevator bolts. The fastener head is normally countersunk below the surface and then capped with a UHMWPE plug to provide a smooth surface.

Resin Compound Types and Properties. This resin is sold as a fine powder, either in natural form or containing a small amount of metallic stearate, which acts as a corrosion inhibitor. Fabricators typically process UHMWPE into rods, tubes, boards, or profiles by ram extrusion, and into billets and sheets by compression molding. Injection molding resins are also available. Pigmentation, light stabilization, antistatic, cross-linking, flame-retardant, and thermal/electrical-conductivity formulations, as well as reinforcements, can easily be added to the virgin resin during processing.

Although numerous modifications to UHMWPE can be made with additives and fillers, it is difficult to improve its two outstanding properties, abrasion resistance and impact strength, because no chemical bonding occurs between the resin and the additive. In fact, one must consider the amount of decrease of either property that can be tolerated. Normally, any modification made to satisfy the application requirements compromises properties. Because the resin is viscoelastic, any additive must be homogeneously mixed prior to processing. Furthermore, the particle size distribution of the modifier should be comparable to or smaller than that of the UHMWPE particles.

Reinforcement. Hardness, creep resistance, dimensional stability, and coefficient of thermal expansion, which is normally 1.5 to 2.0 × 10^{-4}/K, can be improved with the proper selection of reinforcing filler. Wood flour, glass spheres, glass fibers, graphite, aluminum powder, talc, chalk, silicates, and carbonates have been used in concentrations of 5 to 30%. The addition of 5% microglass spheres increases wear resistance and is commonly used for suction box covers in the pulp and paper industry (Ref 5).

Cross Linking and Antioxidants. Chemical cross linking with 0.3 to 0.5% (active ingredient) organic peroxides has been found to improve wear resistance by as much as 30% over nonmodified resins, while reducing deformation under load. Thin-film transparency improves, and density is lowered because of a reduction in crystallinity.

Cross linking can also be accomplished by beta or gamma radiation although polymer chain scission leading to degradation can occur, particularly when radiation occurs in the presence of oxygen. For continued exposure to high temperatures (80 °C, or 175 °F), it is desirable to add 0.1 to 0.2% antioxidant to minimize degradation.

Metal Powder Additives. The heat conductivity of UHMWPE components can be improved by adding metal powders such as copper, aluminum, and bronze. A 400%

increase in conductivity (1.65 versus 0.4 W/m · K) or 11.4 versus 2.8 Btu · in./h · ft^2 · °F) occurs with the addition of 50 wt% (28.5 vol%) aluminum powder. Graphite impr ves thermal conductivity even more efficiently. In both cases, however, toughness and strength are significantly reduced. A mixture of 30 wt% aluminum powder and 10 wt% graphite results in a thermal conductivity of 2.5 W/m · K (17 Btu · in./h · ft^2 · °F) and is used for pile driver pads (Ref 5).

UHMWPE is an effective electrical insulator with a dielectric constant of 2.3 at 2 MHz. The surface resistivity of the natural resin is greater than 10^{13} Ω. It can be reduced to the antistatic region (10^9 to 10^6 Ω), a level required for many mining applications, by the addition of 5 to 6.5 wt% conductive carbon black. Concentrations of 15 to 20 wt% carbon provide resistivities in the conductive range of less than 10^3 Ω.

UV Resistance. The addition of light-absorbing substances provides UV light resistance, with 2.5% carbon black being the most commonly used additive. When the finished product cannot be black, satisfactory UV resistance, which is a minimum of 5 years, can be obtained by 0.5 wt% stabilizer.

Pigments and Lubricants. UHMWPE is typically sold in its natural color, which is opaque white. However, it can be produced in any color with the proper selection of organic or inorganic pigments. Normally, 0.1 to 0.3 wt% is sufficient to obtain good color. Silicone oil, waxes, greases, and molybdenum disulfide (normally, 2 to 5 wt%) can be added to UHMWPE to reduce by a slight amount the already low coefficient of friction properties.

Flame Retardants. The flammability of UHMWPE is similar to that of PE. It ignites readily when in contact with flame and continues to burn when the source of ignition is removed. The addition of a mixture of halogenated and antimony trioxide compounds can reduce its flammability. This addition reduces flame spread by 50% and eliminates flaming drips from the melt. A satisfactory combination of flame retardants will result in an Underwriters' Laboratories V-0 rating.

Resin Suppliers. Domestic resin producers of UHMWPE are Hoechst Celanese Corporation, Houston, TX and Himont USA, Inc., Wilmington, DE.

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